

Chemical bonding in zeolites

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CHEMICAL BONDING IN ZEOLITES

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ABSTRACT. The current status of chemical bonding of zeolites and AlPO's is reviewed. Short range covalent bonding dominates, the tetrahedra have to be considered relatively rigid and the Si-O-Si bond angle flexible. Differences in energy of the SiO₂ or AlPO₄ polymorphs are small. The relative stability sensitively depends on a proper accounting of the small changes in electrostatic energy. The deprotonation energy is also mainly determined by short range covalent interactions. These are only properly accounted for when full lattice relaxation is included in the calculations. Isomorphous substitution effects are also dominated by changes in covalent interaction energy.

1. Introduction

An essential question in zeolite science is the nature of the chemical bond in zeolitic systems. This paper aims to present current understanding and will focus on the covalent as well as electrostatic interactions in these materials. It will appear that structural differences sensitively depend on the balance between the two kinds of interactions. Especially the use of proper quantum-mechanical cluster calculations and the development of new force fields based on such calculations has resulted in a significant improved understanding of zeolite stability as well as the acidity of protonic zeolites that are important for catalytic applications.

The classical zeolites are alumino-silicates. More recent are compounds not based on isomorphous substitution into the SiO₂ unit but containing the [AlO₂-PO₂] dimer as building unit. The past decade has seen considerable progress of theoretical methods able to predict the structure, energy as well as some physical properties of zeolitic materials. For an introductory review we refer to an earlier paper [1]. The large unit cell size currently precludes direct application of first principle quantum-chemical techniques to this problem in solid state chemistry. Especially for the study of chemical reactivity in zeolites [2] application of accurate quantum-chemical methods is highly relevant and fortunately rapid progress is being made. Here we will mainly discuss progress in the development of structure determination, based on the optimization of structures by the use of energy minimization techniques [3] using classical potentials. These lattice energy calculations are based on the rigid ion and the shell model, that we discussed before [4]. An important new development is the generation of a new class of potentials, the partial charge model [5,6], that is a significant improvement compared to the conventional rigid ion potential using formal charges. It's main merit is that a proper balance has been found for the relative contributions of covalent and ionic interactions to the chemical bond. This is the result of the adaptation

of *ab-initio* potential parameter sets generated for small models clusters to requirements of the solid state. The determination of covalent and electrostatic parameters for classical potentials to describe potential energy surfaces generated by quantum-chemical cluster calculations is not a unique procedure. The partial charge model determines the potentials with the additional requirement that physical properties of simple materials as quartz (SiO_2) or berlinite (the AlPO_4 analogue of quartz) are reproduced accurately.

It turns out that the details of structures with the same framework topology sensitively depend on the partial charges chosen for lattice cations and anions. The difference in relative stability of α - and β -quartz are an example [7]. In view of our interest in the zeolitic chemical bond, the overabundance of potential parameters and the need to properly balance the electrostatic and covalent interactions, a comparison of several predicted and experimental properties is essential. By doing this an accurate determination of potential parameters has become possible.

Especially the elasticity constant and bulk compressibility are physical parameters that are very sensitive to structural changes. As we will see experimental information of these properties has been essential to progress in this field [8]. A direct probe for the electrostatic interaction in a material is the splitting of longitudinal and transversal phonon frequencies [4]. The partial charge model reproduces the latter quite satisfactory [5,6]. Quantum-chemical *ab-initio* methods predict stretching frequencies with an accuracy of ten percent, but, as is known for molecules [9], require substantial configuration interaction procedures in order also to reproduce bending frequencies. Prediction of experimental spectra with many group theoretically allowed transitions (as is the case for zeolites with their large unit cell sizes) is only useful with an accuracy of a few percent. For the reproduction and prediction of experimental spectra use can be made of the predicted structures of the partial charge or shell model, but a more refined force field has to be used to compute the vibrational modes. For the SiO_2 lattice the force field developed by Etchepare [10] can be used. For the AlPO_4 structures we recently developed a similar force field [11].

In the section on bond ionicity the partial charge model will be extensively discussed. Applications of force fields for the computation of vibrational modes will be described in the section dealing with relaxation. Whereas in the SiO_2 -system the absolute values of the charges of Si and O are of interest, in the AlPO_4 -system also the distribution of charge between aluminum and phosphorus becomes important. As for SiO_2 polymorphs, also in the AlPO_4 polymorphs the structure sensitively depends on the charge distribution. In layered AlPO_4 structures shifts of the layer positions occur that sensitively depend on the effective charges of aluminum and phosphorus [12]. Also for the acidic zeolites (OH) potentials have been developed [13]. Using these potentials the local distortions of the zeolite lattice due to protonation could be investigated. As we will discuss proper accounting for lattice relaxation is very important when one wishes to study zeolite acidity of protons located in different zeolite lattices.

In the section dealing with structure a comparison will be made of the differences of energies of extended zeolitic lattices with the energies from *ab-initio* calculations on tetrahedral ringsystems. It will appear that energy-differences between zeolitic SiO_2 polymorphs are less than 10 kJ/mole. This is found for the clusters as well as the infinite lattices. Because of the flexibility of the [Si-O-Si] unit, also lattices that develop strain due to connectivity-constraints are able to release this by adaptation of the Si-O-Si angle with very little energy cost [5]. As we have found for the dodecasil-3C lattice this may result in considerable positional disorder. The subject of lattice relaxation will be pursued further

in the two last sections, dealing with vibrational modes and acidity. For the vibrational modes of the faujasite lattice a detailed analysis of these modes in terms of the isolated vibrational ringmodes has been made [14]. This analysis indicates significant redistribution of some ringmodes over the lattice, in agreement with the earlier discussed lattice relaxation. However in specific cases particular ring vibrational modes maintain a high amplitude also in the lattice. The amount of vibrational delocalization becomes small for small Si-O-Si angles and increases with angle. Also the distribution of the kinetic energy over different atoms for particular mode frequencies can be used as a structural probe. This has been used to determine proton positions in zeolites [15].

As mentioned earlier lattice relaxation also has a significant effect on acidity [13]. Brønsted acidity is to a significant measure determined, rather by covalent than electrostatic interactions. The proton has a strong covalent bond with the lattice, resulting in a structural deformation, because of the flexibility of the lattice. Comparison of changes in the vibrational spectrum upon deprotonation of zeolite with computed vibrational mode changes from quantum chemical cluster calculations confirms the covalent bonding type changes [16]. The importance of covalent bonding for understanding the protonation energies of SAPO's will also be discussed [16]. Protonation of substrates has been analysed in earlier papers, but is also still a subject of ongoing research. At the moment the question of the relevance of lattice embedding effects, especially the importance of the differences between electrostatic fields in bulk zeolites and in cluster calculations, can not be considered to be definitively solved.

2. Bond ionicity

Generally the chemical bond strength can be analysed in terms of repulsive and attractive interactions. Equilibrium is established by the balance of these interactions. On a microscopic scale the positive nuclear charges and negative electronic charge distributions never completely cancel even for homonuclear systems. Hence the interaction between chemically bonded atoms cannot be uniquely separated in terms of the covalent and electrostatic contribution and one may even question whether it is useful. This is different for the interactions between non-bonded atoms. Whereas the interaction between neutral systems decreases with a potential $\frac{1}{r^n}$ ($n > 1$), between charged systems the long range potential behaves as $\frac{1}{r}$. This may lead to very slow convergence of long range interactions. Physically the long range electrostatic interactions result in an effective electrostatic field that gives rise to a splitting of the longitudinal and transversal vibrational lattice modes. For an introductory discussion we refer to ref. 4 where also the rigid ion and shell models are introduced and analysed. Here we will limit ourselves to the partial charge model. This recently developed potential representation has been generated on the basis of *ab-initio* quantum-chemical calculations and involves a division of the potential in terms of covalent short range interactions and longer range electrostatic interactions. The choice of effective charges on the atoms requires simulation of the bulk lattice properties. The relative energies of the tetrahedral three dimensional networks, as the SiO_2 - or AlPO_4 -polymorphs are sensitive to a proper choice of the balance of electrostatic versus covalent interactions. The sequence in lattice stability of different structures depends sensitively on this choice. We will illustrate this for the difference in stability of α - β quartz modification. This also elucidates the choice of the effective charges. The general form of the two body potential chosen is:

$$V_{ij}(r) = A_{ij}e^{-b_{ij}r_{ij}} - \frac{C_{ij}}{|r_{ij}|^6} + \frac{q_i q_j}{|r_{ij}|} \quad (351)$$

Ab-initio potential energy surface of neutral cluster as $\text{Si}(\text{OH})_4$, but also for the charged $\text{Al}(\text{OH})_4^-$ and $\text{P}(\text{OH})_4^+$ clusters are fitted by a sum of two body potentials of the type. This fit cannot be unique, because of an overabundance of parameters. A procedure was developed that determined parameter sets for different values of q and b [5,6].

Using a selected parameter set an energy minimization for a particular lattice can be performed [3]. In the partial charge model not formal ionic charges but fitted values are used. The lattice energy minimization procedure enables a prediction of lattice positions and angles by using iterative steps in which lattice positions and angles are changed until the lattice energy is minimized. When this procedure is repeated for the different parameter sets, one finds that only for a particular choice of b and q parameters the α -quartz structure becomes the stable conformation. This behaviour appears to be very general. Figure 1 illustrates this for the calculated bulk compressibility as a function of q for different dense SiO_2 -polymorphs. One notes the phase transition once a particular value of q is exceeded. The transition-point is slightly different for a topologically different structure, but close to $q_{\text{Si}} \approx 2.4$. The bulk compressibility is very sensitive to structure and hence probes structural transformations. Values of q close to the transition point lead to very small differences in energy of different structure modifications for lattices of the same connectivity. The low temperature of the α - β quartz transition, but also the many different temperature dependent modifications found for the other lattices indicate this to be the case.

Quantum-chemical calculations show that the charge distribution between Si and O sensitively depends on the Si-O-Si angle as well as Si-O distance, hence in actual lattices

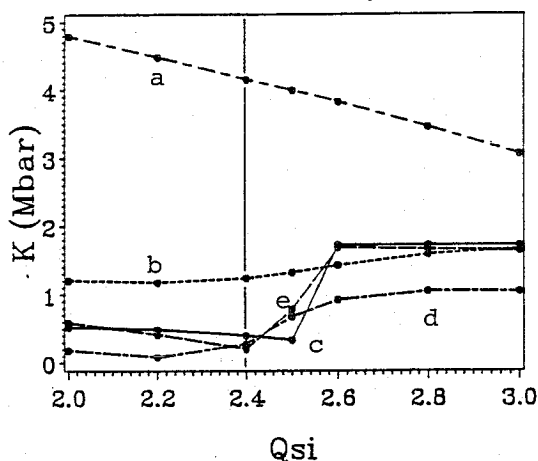


Figure 1. Bulk compressibility as a function of q . a: Stishovite; b: Coesite; c: Quartz; d: Silicalite; e: Cristobalite [7].

small charge differences may be responsible for differences in lattice stability and may change with temperature. In agreement with suggestions by Mortier [17], these differences may be of the order of 0.05 to 0.1 e.u.

A similar analysis has been made for the AlPO_4 lattices. An additional charge parameter in the AlPO_4 lattice is δQ , the effective charge difference of the lattice aluminum and phosphorus ions [5,6]. Using an analogous procedure as for α -quartz, the bulk compressibilities of different AlPO_4 polymorphs can be computed as a function of δQ [12]. In figure 2 results are shown using oxygen potential parameters similar to those used for α -quartz. For some AlPO_4 -polymorphs again a phase transformation type behaviour is observed. These transformations correspond to shifts of layers in the layered AlPO_4 -structures. For AlPO_4 -8 this shift has been experimentally observed [18]. One concludes that $\delta Q > 0.6$. The shifts of the layers result in a puckering of the AlPO_4 channels, which leads to a decreased effective pore diameter.

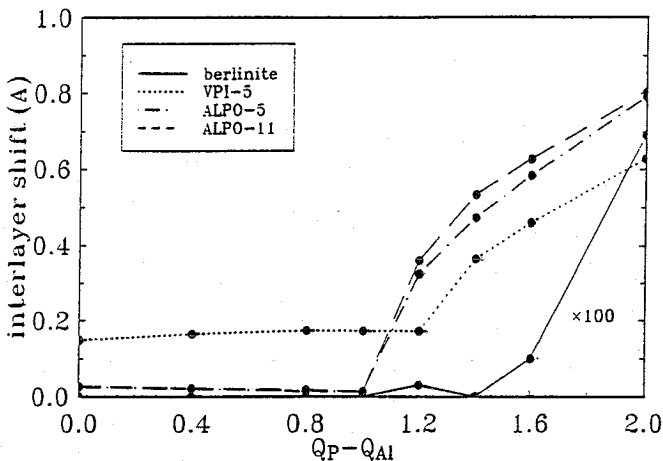


Figure 2. Phase transformation of $AlPO_4$ [12].

3. Structure

As discussed in the previous section physical properties usually sensitively depend on predicted structure or on potentials used. Apart from direct structural determination methods NMR and Infrared spectroscopic measurements are useful techniques because of their easy applicability. We have discussed earlier the use of infrared spectroscopic data to probe different potential models [4].

It appears that complex structures have many saddle points on their potential energy surface. They are not recognized as such in the lattice energy minimization method. However the lattice can only be considered to be in a stable minimum when all computed vibrational frequencies are real. In order to determine stable minima the following procedure is followed. Energy minimization of a lattice is initiated by taking experimental structural data. Usually one finds that these coordinates do not correspond to a theoretical minimum and the iterative procedure to find an energy minimum is started. For a complex structure, different minima are found dependent on the starting configuration. Once a minimum is found the vibrational modes ($\vec{k} = 0$) are computed. Sometimes imaginary frequencies are found. Using the corresponding vibrational mode to distort the "minimum" structure a new starting configuration for the energy minimization is obtained and the procedure is repeated until a stable minimum is found. This method has been very useful for the discovery of the layer displacements in the $AlPO_4$ -structures mentioned before [12], and the analysis of the structure of dodecasil-3C [8]. We will discuss the study of the latter system as an example here.

The dodecasil-3C is a non-zeolitic tectosilicate. It is a SiO_2 polymorph consisting of a unit cell of 34 TO_2 tetrahedra, that encloses cavities (figure 3a). The system is of interest because it is the only low density SiO_2 -structure for which elasticity constants have been measured.

The elastic constants have been measured at room temperature using Brillouin scatter-

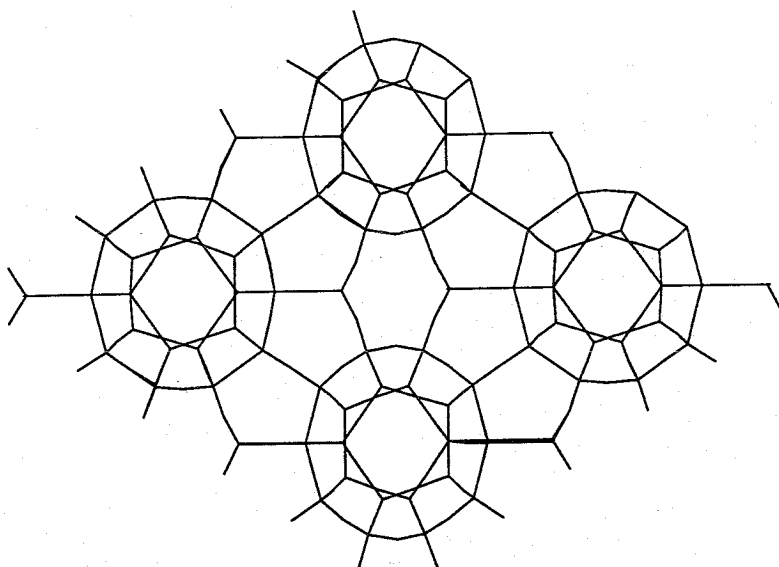


Figure 3. Structure of shell model relaxed dodecasil-3C [8].

TABLE 1. Elastic constants of cubic dodecasil-3C.

	Experiment	Rigid Ion	Shell	Partial Charge
C_{11}	5.5	15.994	19.216	20.114
C_{12}	1.1	5.592	10.755	11.812
C_{44}	2.4	5.222	4.195	4.052
K_0	2.6	9.06	13.58	14.58
Anisotropy	1.1	1.002	1.003	1.007

ing and indicate cubic symmetry [8]. However a simulation starting with a cubic symmetric structure using the three potential models available (rigid ion, shell model and partial charge model) results in major discrepancies between experiment and theory (table 1). Analysis of the vibrational modes of the shell as well as partial charge model simulation indicates the presence of destabilizing imaginary modes. One of them is shown in figure 4 with an arbitrary amplitude of displacement. Results for the double relaxed, stable structures predicted on the basis of the shell and partial charge model are presented in table 2. Non-cubic lattices are finally found. However the agreement between predicted and measured elastic constants has become much better.

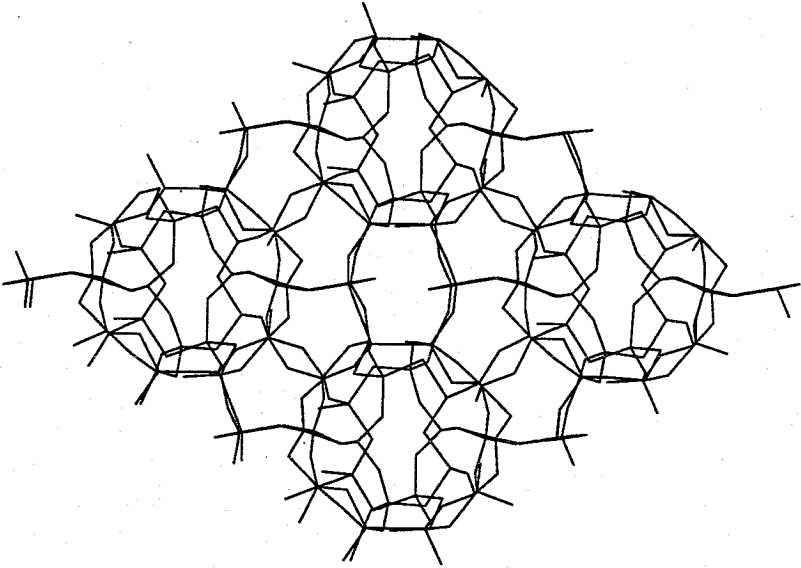


Figure 4. Vibrational mode in dodecasil-3C with an imaginary frequency [8].

It is of interest to compare also simulated and experimental ^{29}Si solid state NMR spectra (figure 5). Experimentally it appears that the dodecasil-3C structure undergoes phase transitions as a function of temperature and also as a function of template present in its cavities. The experimental NMR spectrum of a cubic structure at 373K is similar to the spectrum predicted using the partial charge doubly relaxed structure. The shell model structure appears to agree with an unknown low temperature structural modification. These results illustrate the subtle energetic differences between the structures and how results based on different potentials reflect this. The shell model result would be reproduced by the partial charge model if slightly larger partial charges were used. The computational results can only be reconciled with the overall cubic structure as deduced from elasticity measurements and optical isotropy, by assuming positional disorder with local unit cell deformations corresponding to the theoretically predicted shell model triclinic deformation. This hypothesis is consistent with predicted and measured oxygen atom thermal ellipsoids [8]. The structural disorder as found for the dodecasil-3C structure may be a very general feature of zeolitic materials.

TABLE 2. Elastic constants after double relaxation of cubic structure.

	Experimental	Shell ⁽¹⁾	Partial Charge
C ₁₁	5.5	7.468	7.777
C ₂₂		7.639	7.777
C ₃₃		8.651	12.284
C ₁₂	1.1	1.493	-0.042
C ₁₃		1.144	2.098
C ₂₃		1.170	2.098
C ₄₄	2.4	3.452	3.250
C ₅₅		3.201	3.250
C ₆₆		3.297	3.973
K ₀	2.6	3.48	3.61
A	1.1	1.242	1.597

(1) The shell model is triclinic with $\alpha=89.47^\circ$ $\beta=89.87^\circ$ $\gamma=90.07^\circ$

4. Relaxation

Cluster calculations indicate that motion around the Si-O-Si angle ϕ costs little energy (expansion of the angle from 130° to 180° costs less than 10 kJ/mole), whereas deformation of the O-T-O angle requires a significantly higher energy [20]. Consequently often a wide range of Si-O-Si angles is observed. Strain generated by local distortions can be easily relaxed by adjustment of the Si-O-Si angles. Local distortions may be due to isomorphous substitution of lattice cations, interaction with channel molecules or proton attachment as in acidic zeolites.

Recently for many different SiO₂ and AlPO₄ polymorphs the lattice energies of energy minimized structures have been calculated. The smallest energy differences are found using the results of the partial charge model [5,6]. They are in accordance with experiment [21]. It appears that the SiO₂ structures containing rings with four, five or six tetrahedra have an energy content not differing by more than 10 kJ/mole. This is due to release of strain by adaptation of the Si-O-Si angles. The same is found for the four and six ring containing AlPO₄ structures. For systems containing three rings consisting of three tetrahedra, complete relaxation of strain by adaptation of the Si-O-Si angle is not possible any more, but now also deformation of the O-Si-O tetrahedra occurs. As a result such structures become less stable [5,6,20].

As discussed extensively elsewhere [4] quantum chemical cluster calculations indicate that replacement of Si by Al leads to altered bond lengths and angles. The Al-O bond lengths are larger than the Si-O bond lengths, but also changes in bonding occur outside the direct bonds with Al. This can be understood on the basis of the bond order conservation principle and indicates the importance of covalent bonding in the alumino-silicates. Attachment of a proton to the bridging [Al-O-Si] oxygen atom, leads to a weakening of the

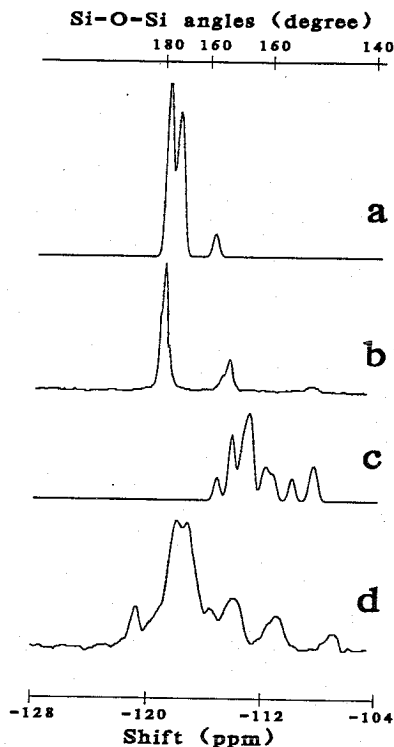


Figure 5. Simulated NMR spectra of dodecasil-3C [8]. a: Calculated from the doubly relaxed partial charge model structure using its Si-O-Si angle distribution; b: Experiment [19] at 373 K; c: Calculated from the doubly relaxed shell model structure; d: Experiment [19] at 213 K.

Al-O and Si-O bonds, also indicative of strong covalent bonding. Using partial charge potential calculations, it has been demonstrated [13] that in extended lattices these deformations remain local distortions, that extend over not more than two neighbouring tetrahedra. Experimental and theoretical evidence for the actual occurrence of lattice relaxation can be found from a comparison of lattice infrared spectra and theoretical simulations. In figure 6 the infrared active lattice frequencies are shown for zeolite in the ammonium form and after desorption of ammonia. In the latter case protons are attached to the zeolite-lattice. Two important changes are observed. Firstly upon protonation the spectral features between 700-1200 cm^{-1} undergo a shift upwards. Features between 500 and 700 cm^{-1} are found to disappear. These features have large amplitudes on the double six ring modes. Computed faujasite lattice modes can be projected on double six ring vibrational modes. The computed amplitudes are plotted as a function of the respective vibrational frequencies in figure 7 [14]. One notes considerable delocalization, but also relatively large amplitudes especially in the "quartz-gap" spectral region [22], where significant mixing of O-Si-O

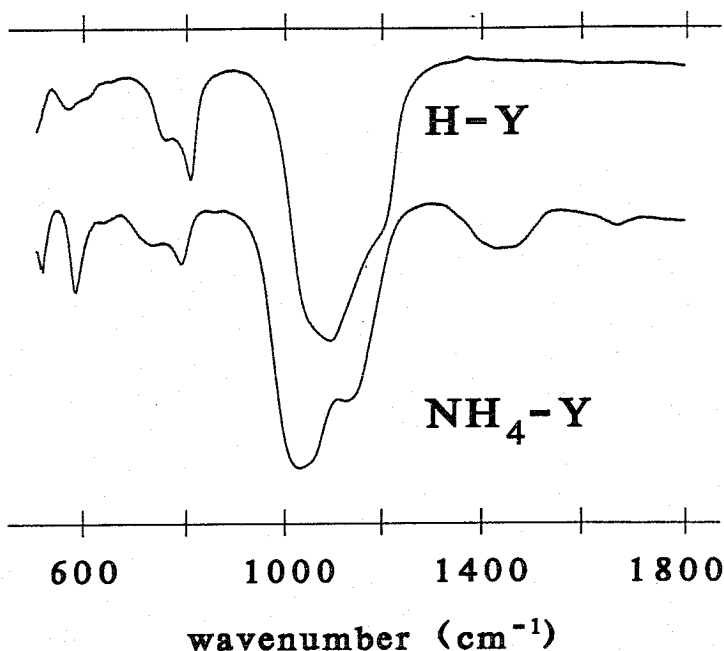


Figure 6. Infrared lattice vibrations of $\text{NH}_4\text{-Y}$ and H-Y [15]

bending and Si-O stretching modes occurs.

Figure 8 shows computed average oxygen atom vibration amplitudes of the infrared active modes. The mode at 620 cm^{-1} is dominated by a motion of the O(3) atom, whereas the lower mode at 516 cm^{-1} is dominated by motion of the O(1) atom. Clearly these two atoms are candidates for protonation. Interestingly this prediction agrees with experimental neutron-diffraction results [23]. The average upwards shift at frequencies larger than 700 cm^{-1} is to be assigned to the average change in Si-O stretch frequencies. This average upwards shift is a consequence of the covalent nature of the zeolite chemical bond. Whereas the Si-O and Al-O bonds that connect the bridging oxygen atom to which the proton becomes bonded, weaken, the Si-O and Al-O bonds belonging to the same tetrahedra but not directly involved with the bridging O-H bond strengthen. This is a consequence of the earlier mentioned bond order conservation principle. Indeed, changes in the lattice mode frequency spectrum of tetrahedral four rings of cation composition Si_3Al reproduce the average upwards shift of the frequencies in the Si-O and Al-O stretch frequency regime [15].

The theoretical results of geometry optimized clusters presented in figure 9, have been obtained within a 3-21G basis set. This explains the 10% average increase of theoretical frequencies when compared to the experiment.

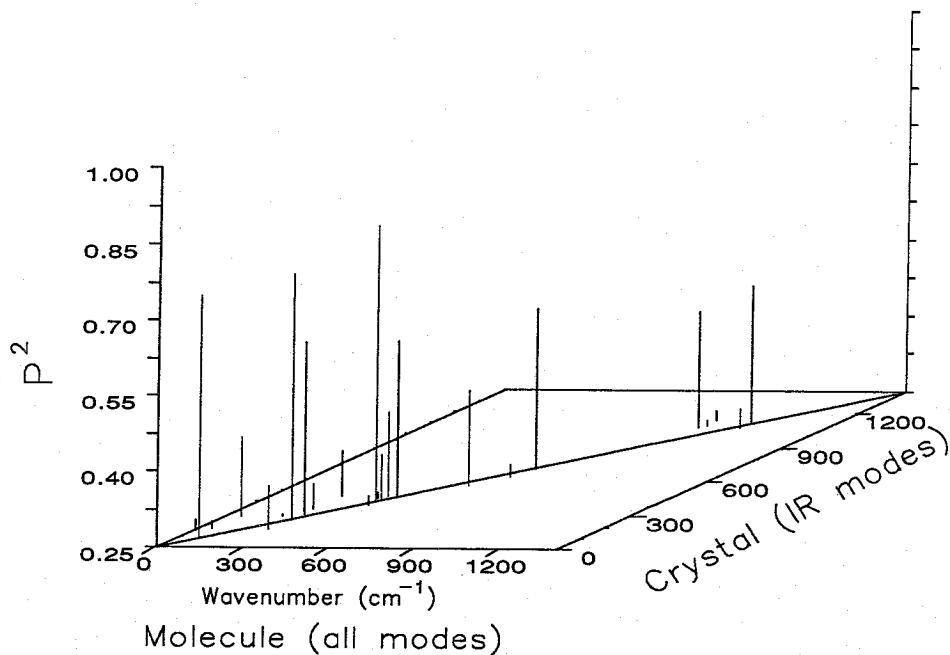


Figure 7. Projections of double six ring modes in siliceous faujasite on modes of molecular double six rings [14]. P^2 is the square of the projection of the normalized vibrational displacement vector of the crystal on the normalized displacement vector of the molecule.

5. Brønsted acidity

Microscopic parameters that are important to acid catalysis are the deprotonation energy of a zeolitic proton and stabilization of protonated molecules [1,4].

Theoretical advances in zeolite acidity mainly originate from the use of high-quality quantum-chemical cluster calculations. As mentioned in the introduction the issue of embedding effects of the cluster into the zeolite lattice still has not been completely resolved. Electrostatic embedding effects become minimized when electrostatically neutral model systems are chosen. Quantum-chemical cluster studies of proton transfer to water [24] or ammonia [25] indicate that in the absence of electrostatic lattice solvation molecules tend to form hydrogen-bonded complexes. Russian workers [26] have suggested for the case of ammonia that the ions can be stabilized by bonding with several protons to the lattice. The ion form then becomes stabilized. The energetic differences reported are small and also the systems studied have not been completely geometry optimized. If issue of mono-dentate versus multi-dentate adsorption of protonated molecules is important to resolve. Whereas the NH_4^+ ion in principle can coordinate with three of its protons directed towards the

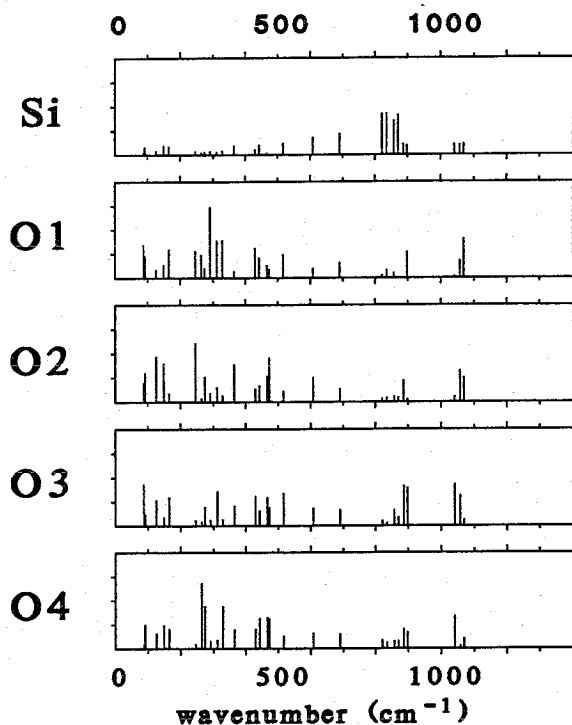


Figure 8. Kinetic energy distribution in siliceous faujasite (Shell model) [14].

lattice oxygen ions, a molecule as pyridinium can only direct one nitrogen bonded proton to a lattice oxygen ion. This may explain the weaker bond strength of pyridinium compared to ammonium with zeolites. Note that in solution pyridine is considered a stronger base than ammonia. Currently several groups are involved to resolve the embedding problem.

More easy is the study of the deprotonation energy. From the previous paragraph it has become clear, that this can only be usefully studied by comparing geometry-optimized clusters before as well as after deprotonation. An important question is how the deprotonation energy depends on zeolite lattice composition. Experimental studies have indicated that zeolite composition effects are of short range nature and are only of importance when the composition of tetrahedra next to the [Si-O-Al] unit changes [27]. Table 3 gives a compilation of deprotonation energies computed from energy differences of protonated and non-protonated rings containing four tetrahedra. The system has been constrained to a planar cation geometry. Calculations have been done using a STO-3G basisset and pseudopotentials. For a few cases the calculations have been repeated using the more accurate 3-21G basisset without pseudopotentials. These calculations confirm the trends found

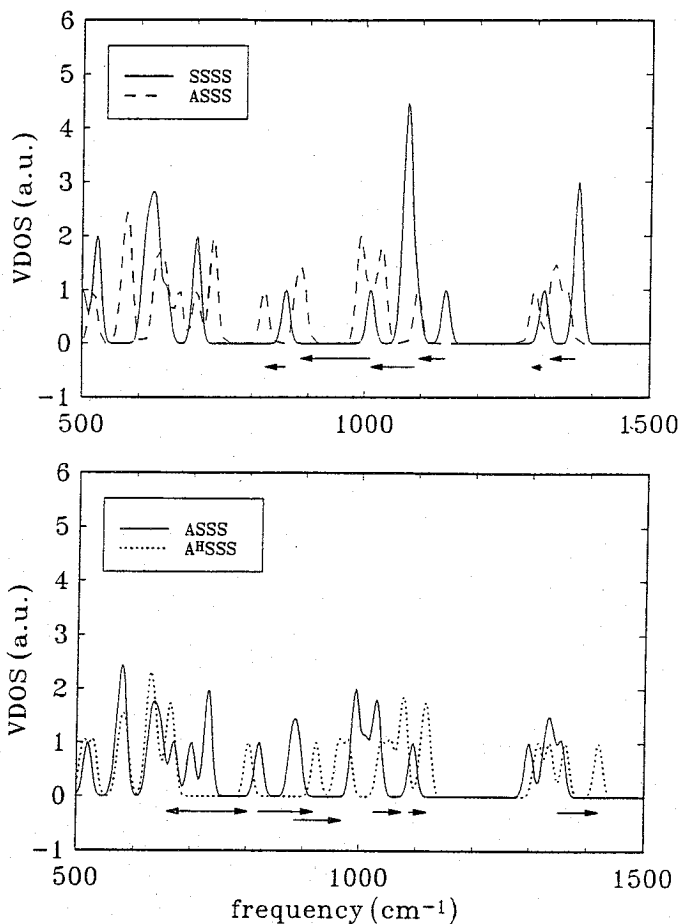


Figure 9. Vibrational density of states of four-ring clusters. SSSS= pure silica cluster; ASSS=one Al substituted cluster; A^HSSS=protonated Al substituted cluster [16].

from the minimum basisset calculations. Rings are compared containing one Al and two Al atoms. Also rings simulating the $[\text{Si}-\overset{\text{H}}{\text{O}}-\text{Al}]$ unit embedded in the AlPO_4 lattice have been studied. Several interesting conclusions follow from these calculations. Proton attachment on bridging oxygen atoms attached to neutral $[\text{Si}-\text{O}-\text{Si}]$ or $[\text{Al}-\text{O}-\text{P}]$ units is always energetically unfavourable. Deprotonation is disfavoured when a $[\text{Si}-\text{O}-\text{Si}]$ unit is replaced by an $[\text{Al}-\text{O}-\text{P}]$ unit or a $[\text{Si}-\text{O}-\text{Al}]$ unit. These changes agree with experimentally observed trends and confirm that covalent bonding effects, rather than changes in electrostatics determine changes in Brønsted acidity. Dwyer [27] has shown that deprotonation energy is a strong function of the Si-O-Al angle ϕ . Indeed calculations, without cluster

TABLE 3. Energies of four ring clusters.

ring ⁽¹⁾	E (Hartree)	PA (kcal/mole) ⁽²⁾
ASSS	-201.331399	
A ^H SSS	-202.002739	421.27
AS ^H SS	-201.925292	372.67
ASAS	-199.216525	
A ^H SAS	-200.024318	506.89
A ^H S ^H AS	-200.633693	444.64
A ^H SA ^H S	-200.726481	473.75
AS ^H A ^H S	-200.683936	460.40
APAS	-201.867723	
A ^H PAS	-202.433139	354.83
APA ^H S	-202.551771	429.24

(1) A^HSSS denotes a four-ring with a single Al-substitution and a proton attached to the oxygen atom bridging the Al and Si.

(2) Proton Affinity.

geometry relaxation, show that the OH bond strength decreases with increasing angle ϕ . We have discussed above that the Si-O-Si angle is very flexible and also that the geometry of the $[\text{Si}-\text{O}^{\text{H}}-\text{Al}]$ unit changes significantly upon deprotonation. A relaxation that can be easily accommodated by the zeolite lattice [13]. Using the force fields discussed above Kramer *et al.* [16] studied the deprotonation energy of a proton in the 48 proton positions of low-aluminum ZSM-5. Full relaxation of the protonated and non-protonated systems is included. The deprotonation energy is found to vary by 0.8 eV. J. Sauer independently found very similar results based on alternative force fields he developed [28]. These results are quite different compared to those found for the non-relaxed case. Relaxation completely overrules the Si-O-Al angle dependence predicted for the non-relaxed systems. The small deprotonation energy differences found for the relaxed systems seem to be determined by subtle differences in local electrostatic energy. These electrostatic effects clearly are secondary to the covalent effects. This again supports the need for a proper embedding theory for clusters modelling zeolite proton reactivity.

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